EXHIBIT A

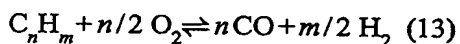# ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY
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3.2. Partial Oxidation of Hydrocarbons

3.2.1. Principle

Partial oxidation is, in principle, the reaction of hydrocarbons with an amount of oxygen insufficient for complete combustion at temperatures between 1600 and 1350 °C and pressures up to 15 MPa. It operates as a continuous process. The basic reactions are as follows:

$$C_nH_m + n/2\ O_2 \rightleftharpoons nCO + m/2\ H_2 \quad (13)$$

$$C_nH_m + nH_2O \rightleftharpoons nCO + (m/2 + n)H_2 \quad (14)$$

$$C_nH_m + nO_2 \rightleftharpoons nCO_2 + m/2\ H_2 \quad (15)$$

The minimum amount of oxygen required for complete conversion of the hydrocarbons is indicated by Equation (13); 0.5 kmol of oxygen is required for every kilomole of carbon. If the reaction proceeds according to this equation, when high-boiling distillates or residual oils (i.e., feedstocks with a large number of carbon atoms per molecule) are being gasified sufficient heat is generally produced to warm the reactants to about 1500 °C. Carbon monoxide and hydrogen are the main products until the hydrocarbons have been completely converted; only then can carbon dioxide and water be formed from surplus oxygen. Opinions differ on the reaction sequence; some test results indicate that carbon dioxide and water are primary reaction products [40].

To prevent excessive temperature increase, steam is usually added, which reacts endothermically with the hydrocarbons according to Equation (14). This leads to the formation of more hydrogen than would be expected from conversion according to Equation (13).

The main elements of the hydrocarbon mixtures — carbon, hydrogen, oxygen, and sulfur — are converted independent of the nature of the feedstock, to the following thermodynamically stable compounds: carbon monoxide, carbon dioxide, hydrogen, water,
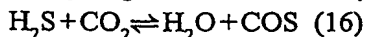
methane, hydrogen sulfide, and carbonyl sulfide. The proportions of various components in the gas mixture are determined by a range of equilibria, which include the shift conversion:
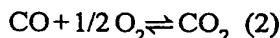
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (7)$$
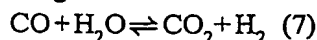
the methane equilibrium:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (8\,a)$$
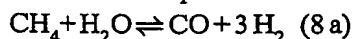
the hydrogen sulfide−carbonyl sulfide equilibrium:

$$H_2S + CO_2 \rightleftharpoons H_2O + COS \quad (16)$$

and

$$CO + 1/2\,O_2 \rightleftharpoons CO_2 \quad (2)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad (11\,a)$$

These equilibria are largely established in the gasification reactor between 1500 and 1350 °C. They remain practically unchanged during very rapid cooling by quenching with water or by indirect heat transfer to water boiling at a comparatively low temperature. Below 900 °C, even an approximation to equilibrium could be achieved only by accepting very long residence times or by using catalysts. The latter cannot yet be applied commercially because of soot formation. The principal advantages of partial oxidation are (1) the possibility of converting hydrocarbons that cannot be vaporized and (2) the complete destruction of all carbon−carbon bonds; the only hydrocarbon remaining in the raw gas is methane.

Methane formation is about ten times as high as indicated by Equation (8 a); this is probably due to the slowness of the reaction according to Equation (11 a). As expected, increasing pressure promotes methane formation; at 1400 °C and 3.0 MPa, the methane content of the product gas is ca. 0.3 vol %, whereas it is 0.55 vol % at 6.0 MPa. Methane content is also influenced by changes in reaction temperature and addition of larger or smaller amounts of steam.

Under conditions prevailing in the reaction zone, no free carbon should be present, according to either the Boudouard equilibrium

$$C + CO_2 \rightleftharpoons 2CO \quad (10)$$

or the reaction

$$C + H_2O \rightleftharpoons H_2 + CO \quad (6)$$
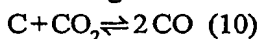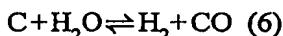
Soot can be present in the raw gas only at below 1200 °C and around 5.0 MPa. Whereas the amount of soot produced during partial oxidation of methane is practically zero, in heavy-oil gasification about 0.5−2.5 mass % of feedstock is contained in the raw gas as free carbon. Some authors assume that this soot formation is due solely to thermal cracking of a proportion of the hydrocarbons; others attribute it partially to the Boudouard limit being reached during cooling. Ash particles in the heavy oils also seem to act as nuclei of condensation or catalysts for soot formation [41], [42].

In heavy-oil gasification, soot formation can be nearly eliminated by increasing the reaction temperature, at the cost of a considerable increase in oxygen consumption and a corresponding increase in carbon dioxide content at the expense of carbon monoxide. Sulfur components of the gas mixture are largely hydrogenated according to Equation (16). Under normal reaction conditions, ca. 95 % of the sulfur is converted to hydrogen sulfide and the remaining 5 % to carbonyl sulfide. No sulfur di- or trioxide is detectable in the raw gas from partial oxidation.